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A Study of the Oxidation of Cymene

A STUDY OF THE OXIDATION OF CYMENE

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Russell Ivan Somers

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A STUDY OF THE OXIDATION OF CYMENE.

I. INTRODUCTION.

The first oxidations of cymene seem to have been carried out to determine whether or not the cymene from different sources was identical. It was soon found that an acid oxidizing agent gave certain products but that an alkaline oxidizing agent gave different results. No investigator seems to have studied the oxidation from the standpoint of the effect of varying the factors affecting the oxidation. The present work on the oxidation of this hydrocarbon was undertaken in order to study as far as possible the different factors, such as concentration of the oxidizing agent, proportions of the oxidizing agent and the hydrocarbon, methods of carrying out the oxidation, etc. which affect the yields of the different products.

II. HISTORICAL.

Noad[(1)] seems to have been the first investigator to produce paratoluic acid from cymene. He treated cymene with dilute nitric acid (one volume of nitric acid- Sp.G. 1.4 - to six volumes of water) and subjected the mixture to repeated distillation. The paratoluic, terephthalic, and nitro acids were then filtered from the well-cooled solution. The paratoluic acid was separated from the mixture by making the barium salt which is easily soluble in water, whereas the barium salts of the other acids are almost

insoluble in cold water. His results indicate that the more dilute the nitric acid used, the purer will be the paratoluic acid obtained.

W. Dittmar and Aug. Kekule [2] used stronger nitric acid as an oxidizing agent. They treated cymene with nitric acid solution (one volume of nitric acid - Sp.G. 1.4 - to four volumes of water) and boiled the mixture under a reflux condenser for several days. After filtering off the acids, they were dissolved in alkali and the nitro acids removed by treating the solution with zinc and hydrochloric acid. The terephthalic and paratoluic acids were then separated by treating the mixture with ether, in which the terephthalic acid is almost insoluble. The paratoluic acid obtained by this method was then subjected to steam distillation in order to free it from a trace of terephthalic acid.

A. Bruchner [3] used practically the same procedure for the preparation of paratoluic acid, except that the paratoluic and terephthalic acids were separated by steam distillation alone.

O. Widman and J.A.Bladin [4] used stronger nitric acid (Sp.G. 1.4) than any of the preceding investigators. With this strength nitric acid, it is necessary to cool the mixture in order to keep it from reacting too violently. By this method, 100 grams of cymene gave, in addition to some paratoluic and terephthalic acids, 60 grams of an oil, which was obtained by ether extraction after the oxidizing solution had been made alkaline. On fractional

distillation some unchanged cymene and a fraction boiling at 222°-224° C. which was paratolyl-methyl ketone, was obtained. Paratolyl-methyl ketone $C_6H_4\begin{cases}CH_3\\COCH_3\end{cases}$ precedes the formation of paratoluic acid in the acid oxidation of cymene.

A.R.Leeds[5] found, while studying the action of nitrogen dioxide, that it reacted with cymene to give paratoluic, and oxalic acids, and a nitrocymene.

Wright[6], and also Bogert and Harris[7] used chromic acid for the oxidation of cymene. Both obtained terephthalic acid from the oxidation. Wright reports a yield of 30%- 35%, while Bogert and Harris report a yield of 45%.

Not nearly as much work has been done on the oxidation of cymene in alkaline solution as in acid solution. Widman and Bladin[4] found that when cymene is oxidized with alkaline potassium permanganate, hydroxyisopropyl benzoic acid, $C_6H_4\begin{cases}CO_2H\\C(OH)\begin{cases}CH_3\\CH_3\end{cases}\end{cases}$ is obtained. This acid is rather soluble in water and is obtained, after filtering off the manganese dioxide, by acidifying the filtrate and extracting the acid from it with ether.

The literature also refers to some special methods of oxidation which have been applied to cymene.

Law and Perkin[8] obtained cuminic aldehyde and a mixture of mono and dihydric alcohols when cymene in dilute sulfuric acid solution was subjected to electrolytic oxidation.

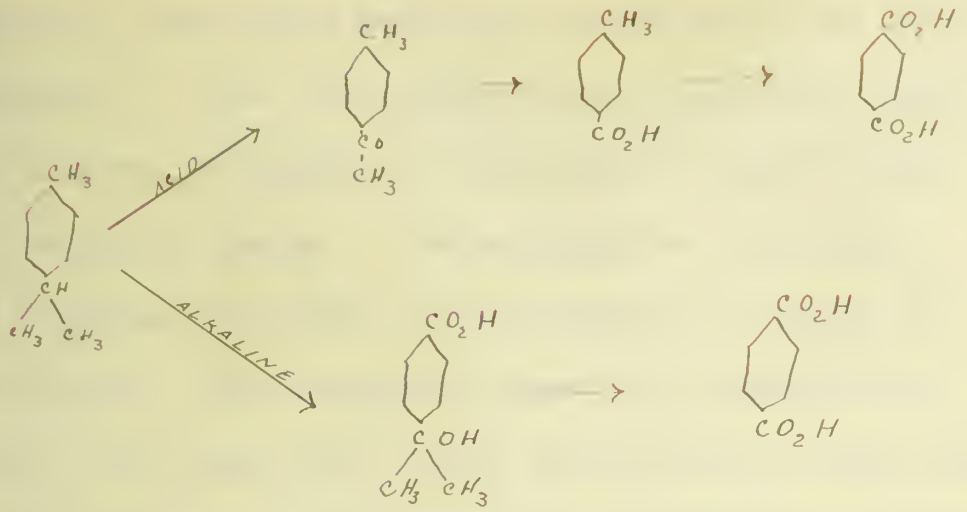
Nencki[9] refers to a private communication which says that cuminic acid $C_6H_4{<}^{CO_2H}_{CH(CH_3)_2}$ is obtained when cymene is shaken with air and sodium hydroxide.

Kingzett[10],[11] reports that when cymene is allowed to stand in contact with the air in sunlight that some oxidation takes place. Paratoluic acid and hydrogen peroxide were obtained.

III. THEORETICAL.

The isopropyl group seems to exert a protective action in some cases, especially in the oxidation of cymene by alkaline potassium permanganate, by electrolytic oxidation, and in the reported oxidation by shaking with air and sodium hydroxide. In all of the above mentioned instances, the methyl group is oxidized first and the isopropyl group is oxidized last or is not attacked at all.

In acid oxidation of cymene, the isopropyl group is attacked before the methyl group. It has been shown[4] that paratolyl-methyl ketone precedes the formation of paratoluic acid. The methyl group of paratolyl-methyl ketone is attacked after the carbonyl group has been oxidized to a carboxyl group, and terephthalic acid is obtained. The following equations show the various stages of the oxidation of cymene in both acid and alkaline solutions.



IV. EXPERIMENTAL.

Oxidation by nitric acid.

An attempt was first made to study the effect of different concentrations of nitric acid when used as an oxidizing agent on cymene.

The following procedure was used: 100 grams of cymene, 282 c.c. of HNO_3 (Sp.G. 1.4), and sufficient water to give the desired concentration were placed in a three-liter flask which was fitted with a mechanical stirrer and a reflux condenser. The mixture was heated on the steam cone until oxidation had apparently ceased. This required from ten to twenty hours and was dependent on the concentration of the nitric acid used. The reaction between strong HNO_3 and cymene is rather violent and in those oxidations where strong HNO_3 was used, the mixture was first heated only until the reaction had started. After the most violent part of the

reaction, the mixture was again heated until the oxidation was completed. After the oxidation was apparently completed, the solution was subjected to steam distillation in order to recover any unchanged cymene. The solution was then filtered while hot. The filtrate was cooled and refiltered to recover the paratoluic acid in it. The precipitate containing terephthalic, some paratoluic , and some nitro acids, in addition to some paratolylmethyl ketone was treated with dilute NaOH until all of the acid was in solution. The alkaline solution was then extracted with ether to remove the ketone and any nitrocymene. The NaOH solution was next acidified and filtered while hot. The precipitate remaining was impure terephthalic acid, and since terephthalic acid can best be purified by esterifying and then hydrolyzing the ester, the terephthalic acid referred to in the following paragraphs will mean the crude product prepared as given above. The filtrate was cooled and any paratoluic acid present filtered off and combined with that previously obtained. The ether extractions from two or three oxidations were collected, and the orange-red oil, obtained on evaporation of the ether, was subjected to fractional distillation.

The following table gives the results obtained by this procedure when using 100 grams of cymene and 282 c.c. HNO_3 (Sp.G. 1.4) diluted to the indicated specific gravity.

TABLE I.

Exp. No.	Sp.G.of sol.	Terephthalic acid.	Paratoluic acid.	Cymene recovered.
1.	1.10	16 grams	17 grams	9 c.c.
2.	1.15	21 "	28 "	2 "
3.	1.20	17 "	26 "	0 "
4.	1.25	21 "	17 "	0 "
5.	1.30	18 "	12 "	0 "
6.	1.35	24 "	26 "	0 "

The ether extractions from experiments 3,4, and 5 yielded 155 grams of an orange-red oil, from which 17 grams of a white crystalline solid separated out on cooling in an ice bath. After filtering, the precipitate was recrystallized from alcohol. It gave a M.P. of 118° C. which corresponds to the melting point of the substance which Fittig,Kobrüch, and Silke called trinitro-cymene.

The filtrate from the above was subjected to fractional distillation. A 6 c.c. fraction with a B.P. of 215°-224° C, which was mostly paratolyl-methyl ketone, was obtained. The fraction boiling at 240° - 245° C. was nitrocymene. The material boiling above 250° C. could not be distilled since it decomposed, even under diminished pressure. The presence of polynitro derivatives is probably responsible for this decomposition.

Several oxidations using a large excess of cymene were made. The procedure, in general, was the same as was followed above. In one case, 100 grams of cymene and 200 c.c. of water was mixed with 77 c.c. con. HNO_3. The HNO_3 used was theoretically sufficient to oxidize one half of the cymene to paratolyl-methyl ketone. After heating the solution for three hours, the following results were obtained : 55c.c. of cymene recovered by steam distillation. The ether extraction gave 40 grams of an oil which on fractional distillation gave 15 c.c. of paratolyl-methyl ketone. The remainder of the oil decomposed. About a gram of paratoluic acid was also obtained.

The effect of an excess of the oxidizing agent was next tried. The results given in the following table were obtained by the method previously outlined except that the amounts of materials used were changed.

TABLE II.

Exp.No	Cymene used.	HNO_3 used.	Sp.G. of solution.	Terephthalic acid.	Paratoluic acid.
7.	50 c.c.	163 c.c.	1.30	15 grams.	8 grams.
8.	50 "	245 "	1.30	17 "	7 "
9.	50 "	245 "	1.15	20 "	14 "
10.	50 "	320 "	1.15	20 "	10 "

In Exp. No. 7, the HNO_3 used was theoretically sufficient to oxidize all of the cymene to terephthalic acid. In Exps. No. 8 and No. 9 a 50% excess of the theoretical amount of

acid necessary was used, and in Exp. No. 10 a 100% excess of the theoretical amount was used.

In the four previous experiments the mechanical stirrer rolled the acid formed and some of the cymene into small hard pellets which were resistant to further oxidation, and therefore some cymene was not oxidized because the oxidizing agent did not have a chance to act upon it. For this reason the oxidation without a stirrer was tried. 25 c.c. of cymene, 450 c.c. of water, and 125 c.c. con. HNO_3 (50% in excess of the theoretical amount to give terephthalic acid) were placed in a flask with a reflux condenser and placed on the steam bath for 60 hours. The above HNO_3 solution had a Sp.G. of 1.10. This oxidation gave a yield of 18 grams crude terephthalic acid, which was 64% of the theoretrical yield, and 2 grams of paratoluic acid. The 18 grams of crude terephthalic acid were treated with 75 c.c. of ether. 15 grams - a 53% yield - of pure white terephthalic acid was obtained.

In order to try to increase the yield of paratoluic acid, 25 c.c. of cymene, 125 c.c. con. HNO_3 and 450 c.c. of water were placed in a flask with a reflux condenser and boiled gently over a flame for ten hours. The solution was diluted with an equal volume of water and filtered hot. The precipitate was treated with a liter of hot water and again filtered. The filtrates were united and cooled, and the paratoluic acid filtered off. The yield was 4 grams of terephthalic acid and 12 grams

of paratoluic acid, which was a 52% yield.

Oxidation by chromic acid mixture.

The oxidation of cymene by chromic acid mixture was carried out according to the directions given by Bogert and Harris[7]. 50 c.c. of cymene, 1300 c.c. of water, 550 c.c. con. H_2SO_4, and 385 grams of $Na_2Cr_2O_7$ were placed in a five liter flask with a reflux condenser and boiled gently for three days. The mixture was then diluted with an equal volume of water and the terephthalic acid filtered off and purified. The yield was 15 grams of terephthalic acid.

Oxidation by potassium permanganate.

The oxidation of cymene by alkaline KMnO was carried out by placing in a three-liter flask fitted with a reflux condenser 20 grams of cymene, 40 grams of $KMnO_4$, 10 grams of NaOH, and 1250 c.c. of water. The mixture was boiled gently until the solution was decolorized. The solution was then steam distilled in order to recover any unchanged cymene. 8 c.c. of cymene were received. The MnO_2 was next filtered off and the filtrate evaporated to a volume of 200 c.c. and acidified with HCl. After cooling in an ice bath, the hydroxyisopropyl benzoic acid was filtered off. 8 grams of this acid, a 50% yield, was obtained. The solution was extracted with 25 c.c. of ether in order to recover any of the hydroxyisopropyl benzoic acid re-

maining in solution. The ether extract gave about .5 gram of this acid.

The next two oxidations varied from the preceding one only in the amount of $KMnO_4$ used. In one 75% excess, and in the other 100% excess of the theoretical amount of the $KMnO_4$ was used. No cymene was obtained in either case on steam distillation. The yields of hydroxyisopropyl benzoic acid were 40% and 47% respectively.

An attempt was made to produce terephthalic acid by acid $KMnO_4$ oxidation of cymene. The following procedure was used. 20 grams of cymene, 2500 c.c. of water, 85 c.c. of con. H_2SO_4, and 62 grams of $KMnO_4$ were placed in a three liter flask fitted with a reflux condenser and boiled gently for ten hours. The cymene disappeared but only a trace of terephthalic acid was obtained. The oxidation was apparently so vigorous that the nucleus was broken.

Attempted oxidation by air and alkali.

An unsuccessful attempt was also made to carry out the oxidation of cymene by shaking it with NaOH and air. 25 c.c. 200 c.c. of water, and 50 grams of NaOH were placed in a 500 c.c flask fitted with a mechanical stirrer and a reflux condenser. After boiling the mixture gently over the open flame for 15 hours, while blowing oxygen through the solution, the unchanged cymene was recovered by steam distillation. The solution was

acidified and extracted with ether. No cuminic acid was obtained.

V. CONCLUSION.

1. These experiments with the nitric acid oxidation of cymene indicate, as other investigators have found, that the isopropyl group is attacked first, and that paratolyl-methyl ketone precedes the formation of paratoluic acid. The methyl group is attacked only after the isopropyl group has been changed to a carboxyl group.

2. A solution of nitric acid of Sp.G. 1.10 - 1.15 gives more oxidation and less nitration than either a stronger or weaker solution, and in addition the reaction between cymene and nitric acid of the above strength goes quietly and smoothly.

3. The best results for the preparation of terephthalic acid were obtained when at least a 50% excess of the theoretical amount of nitric acid was used.

4. Terephthalic acid is best obtained by heating the oxidizing mixture on the steam cone for several days; on the other hand, paratoluic acid which is an intermediate stage is obtained in the largest amount by boiling the oxidizing mixture gently for about ten hours, or until most of the cymene is gone and not long enough to oxidize the paratoluic acid to terephthalic acid.

5. Oxidation of cymene in alkaline solution by potassium

permanganate gives hydroxyisopropyl benzoic acid. In acid solution this oxidizing agent is so vigorous that the nucleus is broken.

6. Terephthalic acid is produced by the action of chromic acid solution on cymene. This oxidizing agent is so vigorous that the oxidation cannot be stopped at any of the intermediate stages.

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